

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Investigation of single crystal silicates for blue tunable lasers		5. TYPE OF REPORT & PERIOD COVERED Quarterly No. 1 Dec. 1, 1985 Feb. 28, 1986
7. AUTHOR(s) R, F. Belt & J. A. Catalano		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Airtron Division, Litton Industries 200 E. Hanover Ave Morris Plains, NJ 07801		8. CONTRACT OR GRANT NUMBER(s) N00014-85-C-0823
11. CONTROLLING OFFICE NAME AND ADDRESS Defense Contract Administration Service 240 Route 22 Springfield, N.J. 07081		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Project 410 NR 392-053/4-19-85
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Office of Naval Research Department of the Navy 800 No. Quincy Street Arlington, Virginia 22217		12. REPORT DATE June, 1986
		13. NUMBER OF PAGES 19
16. DISTRIBUTION STATEMENT (of this Report)  Approved for public release: distribution unlimited.		15. SECURITY CLASS. (of this report)  UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)  None		
18. SUPPLEMENTARY NOTES  None		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)  Tunable lasers Rare earth silicates Czochralski growth Laser crystals		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  The single crystal growth of rare earth silicates was investigated for the purpose of tunable laser hosts. Silicates of the type $R_2SiO_5$ , where $R = La, Gd, Y$ , were prepared from stoichiometric melts and doped with $Ce^{3+}$ activators. Seed crystals were obtained from crystallized melt sections or by growth on an iridium wire.		

Cathodoluminescence experiments on both powders and single crystals showed wavelength shifts with different rare earth ions. The Gd, Y, and mixed crystals of Gd-Y silicates gave good bright emission with  $Ce^{3+}$ . The emission is broad band and covers the wavelength range of 370-525nm. The peak emission can be centered near 450-460 nm by other compositions. Larger single crystals for laser hosts are under development.

Unclassified

INVESTIGATION OF SINGLE CRYSTAL  
SILICATES FOR BLUE TUNABLE LASERS

by

✓ R.F. Belt and J.A. Catalano

Quarterly Report No. 2  
December 1, 1985 - February 28, 1986

Airtron Division  
Litton Industries, Inc.  
//200 East Hanover Avenue  
Morris Plains, New Jersey 07950

June~~x~~ 1986

NOTICES

Approved for public release; distribution unlimited. This research was sponsored by the Office of Naval Research, Department of the Navy, Physics Program, 800 North Quincy Street, Arlington, Virginia 22217. Qualified requesters may obtain copies of this report from Defense Documentation Center, Cameron Station, Alexandria, Virginia 22314. Destroy this report if no longer needed; do not return to sender.

## NOTICES

The findings in this report are not to be construed as an official Department of the Navy position unless designated by other authorized documents.

The citation of trade names or names of manufacturers in this report should not be taken as official Government endorsement or approval of commercial products or services referenced herein.

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever, and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder of any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

## TABLE OF CONTENTS

	<u>PAGE</u>
DD Form 1473	
Table of Contents	i
List of Figures and Tables	ii
Foreword	iii
1.0 Introduction	1
2.0 Experimental Procedures	5
2.1 Feed Material	5
2.2 Czochralski Technique	7
2.3 Cathodoluminescent Evaluation	7
2.4 Optical and Laser Evaluation	9
3.0 Results and Discussions	9
3.1 Phase Diagrams	12
3.2 Doping and Atmosphere Control	12
3.3 Experimental Runs	13
3.4 Cathodoluminescence Results	13
3.5 Optical and Laser Evaluation Results	13
4.0 Conclusions	18
5.0 References	19

# LIST OF FIGURES AND TABLIES

	<u>PAGE</u>
Figure 1 $\text{Gd}_2\text{O}_3$ - $\text{SiO}_2$ Phase Diagram	3
Figure 2 $\text{Ce: Gd}_2\text{SiO}_5$ UV Excited Luminescence Spectrum	6
Figure 3 R.F. Growth Furnace Schematic	8
Figure 4 $\text{Ce: Gd}_2\text{SiO}_5$ - Beam Cathodoluminescence Spectrum	10
Figure 5 Boule Section from Run 23	15
Table I List of Experimental Runs 21 to 23	17

## FOREWORD

This quarterly report describes research efforts on the preparation of single crystal rare earth and other silicate laser hosts. All crystals were doped with  $\text{Ce}^{3+}$  in an attempt to obtain blue or blue-green lasers which may operate near 450-480nm. The report relates work started in the period of December 1, 1985 up to February 28, 1986. All work was done under a program of Dr. Van O. Nicolai of the Office of Naval Research. It is now continuing under the administrative supervision of Dr. Robert Junker of the Office of Naval Research and technical monitoring of Dr. Leon Esterowitz at the Naval Research Laboratory.

All physical preparations were completed in the laboratories of Airtron Division of Litton Industries, 200 E. Hanover Avenue, Morris Plains, New Jersey 07950. The program was directed by Dr. Roger F. Belt and Mr. Joseph Catalano served as Senior Staff Scientist. Mr. Gregory Foundos was the technician. Optical tests were performed at the Naval Research Laboratory through the courtesy of Dr. Leon Esterowitz. The X-ray patterns were run by Mr. John Yorston. Cathodoluminescent tests were performed by Dr. John Ings. The report was prepared by Dr. Roger Belt and Mr. Joseph Catalano. It was released for publication in July 1986.

## 1.0 Introduction

It has been a long term goal of the Navy to obtain high efficiency blue or blue-green solid state lasers. One of many approaches for tunable systems involves the luminescent 5d-4f transitions of  $\text{Ce}^{3+}$ . A major problem has been to find suitable single crystal hosts which have the following features.

1. Chemical and physical properties similar to other good hosts, e.g.  $\text{Al}_2\text{O}_3$ ,  $\text{Y}_3\text{Al}_5\text{O}_{12}$ ,  $\text{YLiF}_4$ .
2. Ability to incorporate  $\text{Ce}^{3+}$ ,  $\text{Pr}^{3+}$ , or other rare earth ions substitutionally.
3. A high band gap of about 6 eV to prevent excited state absorption of  $\text{Ce}^{3+}$ .
4. High radiative lifetime and fluorescence yield of  $\text{Ce}^{3+}$ .
5. The presence of  $\text{Ce}^{3+}$  in a suitable site and symmetry to luminesce at 450-500nm.

Most of the previous work under this program<sup>(1)</sup> has been concerned with the perovskite structured host materials such as  $\text{LaAlO}_3$ . This compound is a distorted cubic crystal which leads to a hexagonal or orthorhombic structure. Efforts to obtain the stable cubic form of the crystal have been largely negative. The crystal of pure  $\text{LaAlO}_3$  gives fluorescence with  $\text{Ce}^{3+}$  but the presence of twins and a phase transformation prevents good laser crystals from being produced. So far no single high quality crystals of cubic perovskites have been grown. Most of the difficulties are associated with phase



behavior, melting points greater than 2000°C, and presence of inclusions or twins. During the course of our work, a few runs of polycrystalline  $\text{Gd}_2\text{SiO}_5$  doped with  $\text{Ce}^{3+}$  were produced for trial fluorescent experiments. This material showed some promise for ultraviolet excited emission and gave a broad band which peaked around 430-470 nm. Since  $\text{Gd}_2\text{SiO}_5$  and other rare earth silicates show some promise for shifting the emission with  $\text{Ce}^{3+}$  doping and can be grown as single crystals, this appears to be a fortunate start for a blue-green laser. The thrust of our research effort was concerned with silicates of the type  $\text{R}_2\text{SiO}_5$  where R = any rare earth or yttrium.

The rare earth silicates are interesting laser hosts which exhibit nearly all of the features of doping, mechanical properties, low cost, congruently melting behavior, and apparently a completely isomorphous structure from La to Lu. A description of various compounds and structures in the  $\text{R}_2\text{O}_3\text{-SiO}_2$  systems is given in a general reference.<sup>(2)</sup> The main compounds are 1:1  $\text{R}_2\text{SiO}_5$ , 2:3  $\text{R}_4\text{Si}_3\text{O}_{12}$  and 1:2  $\text{R}_2\text{Si}_2\text{O}_7$ . A typical phase diagram<sup>(3)</sup> is given in Figure 1; this figure is for  $\text{Gd}_2\text{O}_3\text{-SiO}_2$  but all other rare earths are nearly identical. It is a general feature that only the 1:1 compounds of type  $\text{R}_2\text{SiO}_5$  are all congruently melting with melting points in the range of 1900-2000°C. The remaining 1:2 or 2:3 type silicates are incongruently melting and special procedures must be used to obtain single crystals. Thus it appears that only the 1:1 composition may be grown large enough to yield traditional laser rods of 2-10cm length.

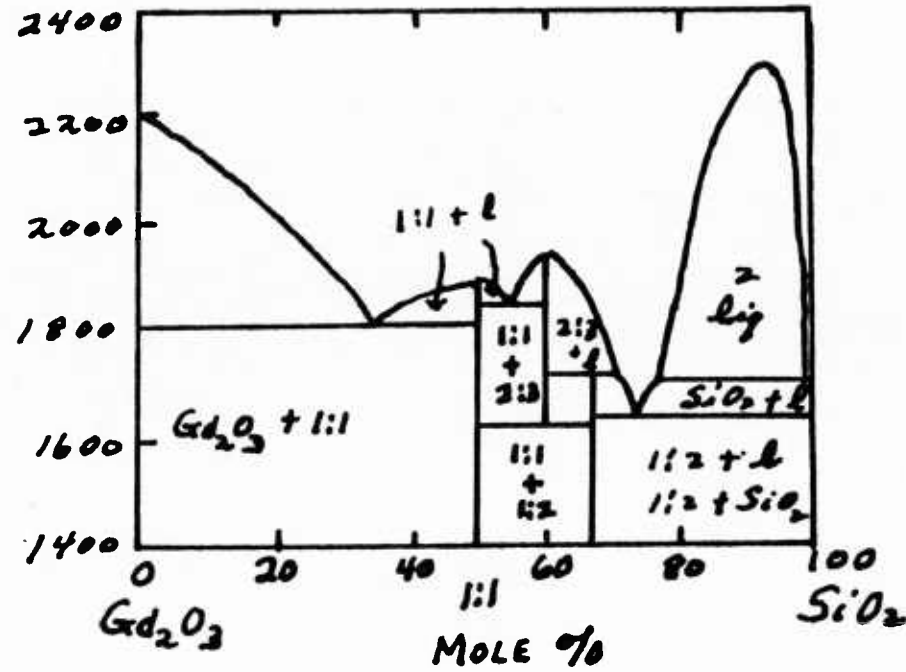


Figure 1 System  $\text{Gd}_2\text{O}_3$ - $\text{SiO}_2$ . Oxide ratios of compounds are given as  $\text{Gd}_2\text{O}_3:\text{SiO}_2$ . (Ref. 3)

The few preliminary studies of rare earth silicate growth were all performed by the flux method.<sup>(4-8)</sup> This method utilizes fluxes such as  $\text{Bi}_2\text{O}_3$ ,  $\text{Li}_2\text{O}-\text{MoO}_3$ ,  $\text{KF}$ ,  $\text{PbO}-\text{PbF}_3$ , or combinations of the preceding to grow a particular composition of silicate. The crystals grown from these fluxes were of mm size and useful for X-ray or other structural studies. In all cases the absorption or emission spectra were not recorded. Neither were there any laser studies performed because of the size of the crystals. No further efforts were described to obtain single crystals for any purpose.

The earliest growth of  $\text{Y}_2\text{SiO}_5$  single crystals was done in conjunction with laser research in the Soviet Union. In 1973 it was reported<sup>(9,10)</sup> that  $\text{Nd}^{3+}:\text{Y}_2\text{SiO}_5$  was lased successfully at 300°K. Rods of mm size were used and the material had a low threshold of a few joules in a pulsed mode of operation. The emission spectrum, threshold, and other laser parameters were highly dependent on the orientation of the crystal axes of the laser rods. It appears that the crystal structure is orthorhombic and the two site symmetries at the  $\text{Y}^{3+}$  may be slightly different. What governs the site preference upon doping for laser action has not been explained. In  $\text{Gd}_2\text{SiO}_5$  doped with  $\text{Ce}^{3+}$ , it may give rise to the small auxiliary peak near 545nm. In any case, a more detailed spectral study is required for the growth and doping of the single crystals.

In 1983, workers in Japan reported<sup>(11)</sup> the Czochralski growth of  $\text{Ce}^{3+}:\text{Gd}_2\text{SiO}_5$  for a scintillator application. These

crystals were 25mm diameter and 40mm long. The luminescence spectrum of the 1.0 atomic percent Ce crystal is shown in Figure 2. The excitation is by 254nm ultraviolet light. It can be seen that the broad band emission has a peak in the blue near 450nm. The substitution of Y for Gd shifts the peak further into the blue near 400nm. While no experiment was performed on La addition, the larger unit cell and reduced crystal field about  $\text{Ce}^{3+}$  will probably shift the peak in the opposite direction, i.e. toward 470-480 nm. The fluorescent lifetime of the  $\text{Ce}^{3+}$  in  $\text{Gd}_2\text{SiO}_5$  is about 60ns. This value is equal to or slightly larger than  $\text{Ce}^{3+}$  in YAG or other oxide hosts.

Further literature on the Czochralski type growth is not available. In November, 1984, a personal visit was made to Philips Laboratories in Eindhoven, The Netherlands. It was learned that this laboratory was growing single crystals of  $\text{Y}_2\text{SiO}_5$  by pulling from the melt.<sup>(12)</sup> The crystals were about 2 x 8 cm and desired for phosphor research. In some previous papers by Philips personnel, the silicates were found to be some of the most efficient phosphors available. The work at Philips also confirms that good single crystals can be grown.

## 2.0 Experimental Procedures

### 2.1 Feed Material

The precursor powders used in these experiments were of 4-9's purity or better. The  $\text{CeO}_2$  was purchased from Spex Industries, Inc., the  $\text{Gd}_2\text{O}_3$  from the United Mineral Corporation, the  $\text{Y}_2\text{O}_3$  from Rhone-Poulenc, and the  $\text{La}_2\text{O}_3$  and  $\text{SiO}_2$  from Johnson Matthey. These powders were weighed to the nearest tenth or

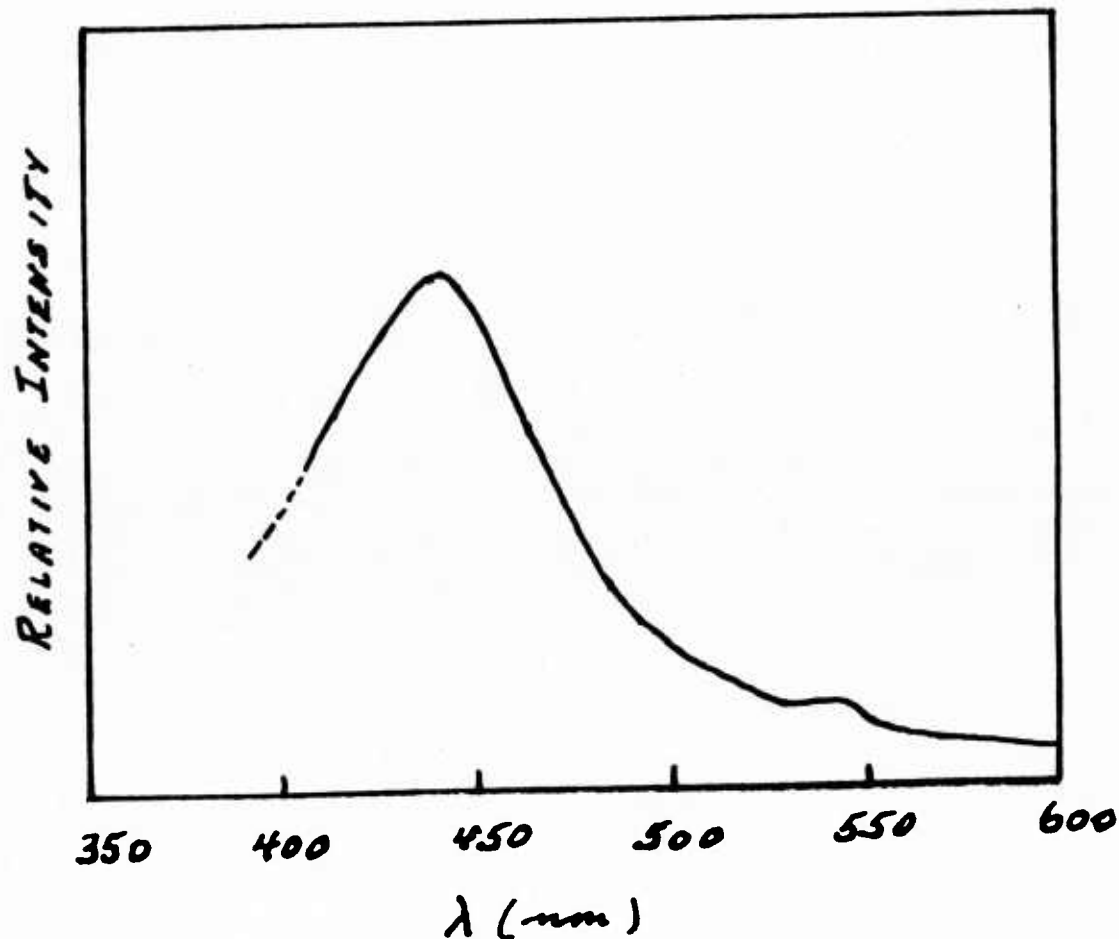


Figure 2 Luminescence spectrum of Ce:Gd<sub>2</sub>SiO<sub>5</sub> single crystal excited by ultraviolet (wavelength 254nm) at room temperature. (Ref. 11)

hundreth of a gram and were then blended together in a polycarbonate plastic divider/mixer for three to four hours. This mixture was then charged via a quartz funnel into the crucible which was at a temperature to cause pre-reaction and sintering of the powdered components. Upon completion of the sintering of the full charge (usually accompanied by partial melting of the charge in the bottom of the crucible) the crucible temperature was raised to above the mixture's melting point where it was held for 24 to 48 hours to ensure complete mixing. Radial flow lines were clearly visible once the melting point of the charge was reached.

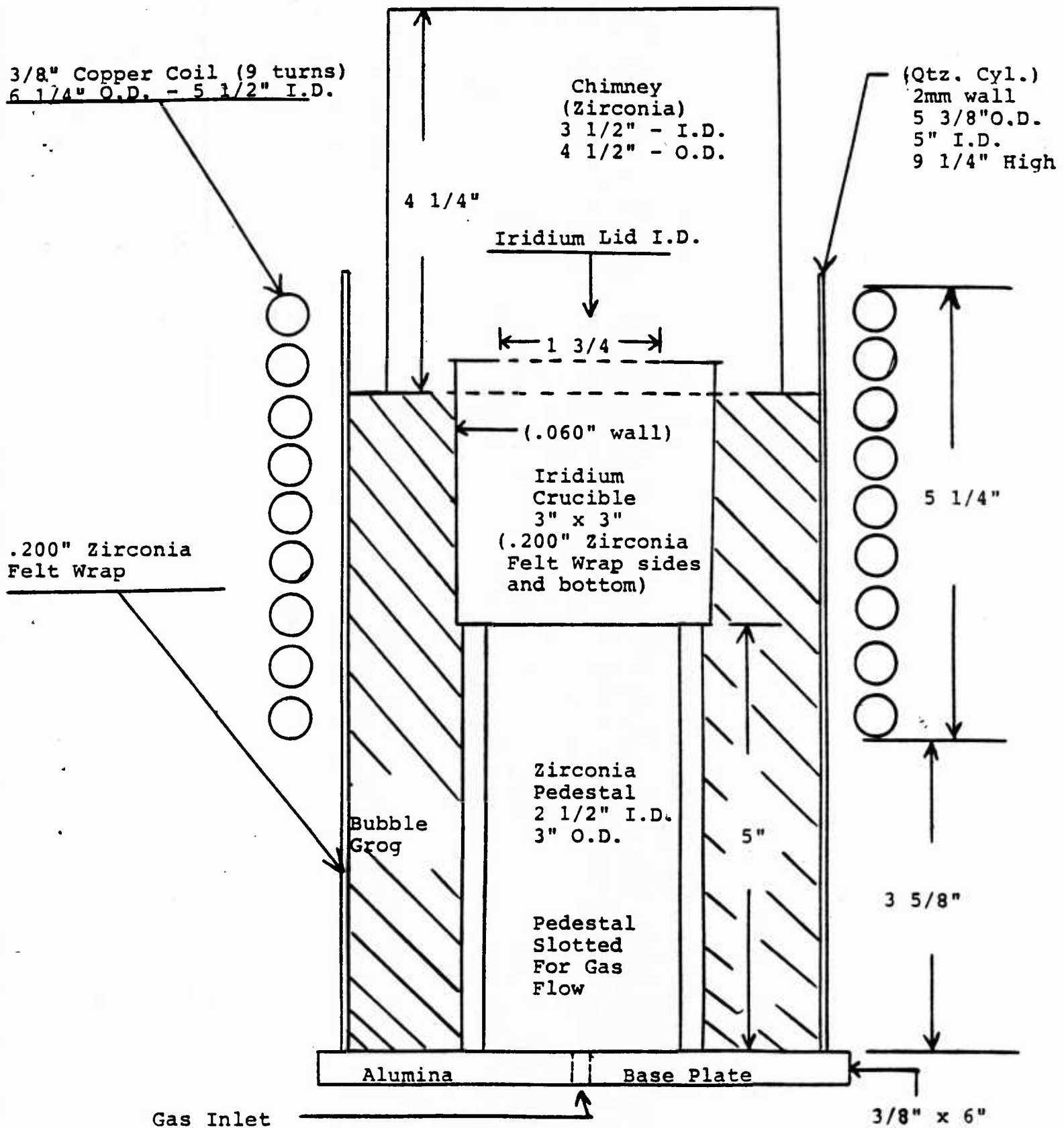
## 2.2 Czochralski Technique

The geometrical arrangement for this series of growth runs is shown in Figure 3. A 3 inch by 3 inch iridium crucible, capped with a 2 inch I.D. iridium lid was used for most of the runs. The crucible is heated by RF coils powered by a 30 kw Lepel generator. The cover atmosphere for each run was high purity nitrogen from a cryogenic source. The gas was fed through holes centered in the steel table and zirconia base plate. The gas then exited from vertical slots cut in the zirconia support cylinder to flow up through the grog. The flow rates were generally in the range of 25 liters/min. The pulling rates and rotation rates are detailed in Table I. Melt drop compensation was employed during runs where a boule was pulled.

## 2.3 Cathodoluminescent Evaluation

Preliminary evaluations for luminescence were done under UV light. If a sample exhibited a visible response then a small

Figure 3 RF Growth  
Furnace Schematic





single or polycrystalline sample was prepared for e- beam excitation. Upon exposure to the e- beam, the sample luminesces due to its  $\text{Ce}^{+3}$  content and this emitted radiation is scanned by a very accurate monochrometer and its intensity versus wavelength profile (from 300nm to 700nm) is recorded on a strip chart. This allows evaluation of the relative strength and peak wavelength position of the  $\text{Ce}^{+3}$  emission spectrum. A typical spectrum for  $\text{Gd}_2\text{SiO}_5:\text{Ce}^{+3}$  is shown in Figure 4.

#### 2.4 Optical and Laser Evaluation

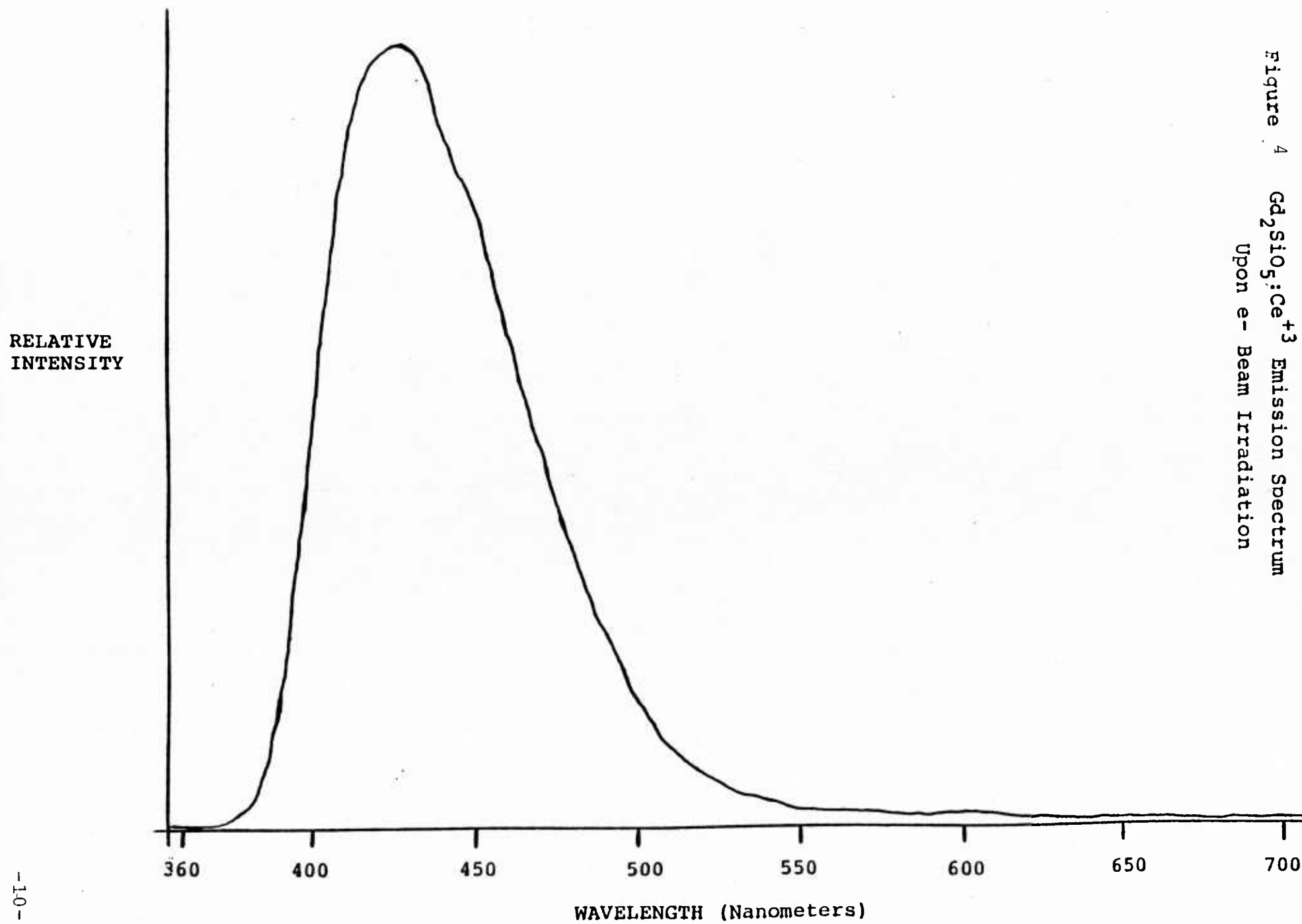
Optical and laser evaluation of samples from successful runs were to be performed at NRL. Samples for this purpose were to be prepared at Airtron by cutting single crystal sections from each boule and polishing them to optical clarity.

#### 3.0 Results and Discussion

Since it appears that all the rare earths (R) form an isomorphous series in the compounds  $\text{R}_2\text{SiO}_5$ , the crystal grower is presented with tremendous latitude in the preparation of both hosts and dopants for laser application. Let us consider the host crystal first. The elements La, Gd, Y and Lu span the full range of rare earth radii. Furthermore, each of these elements or their mixtures have trivalent ions with half or full shell electron complements; thus they are fully transparent in the absence of defect chemistry. The choice of  $\text{Gd}_2\text{SiO}_5$ , which was grown first, is in the middle of the rare earth series. Doping with  $\text{Ce}^{3+}$  gives emission near 450nm. If Gd is mixed with Y, the emission should shift more towards the blue. If one mixes La and Gd, the peak emission may shift towards the red. By tailor-



Figure 4  $\text{Gd}_2\text{SiO}_5:\text{Ce}^{+3}$  Emission Spectrum  
Upon e- Beam Irradiation



ing the type of mixed crystal, it should be possible to shift  $\text{Ce}^{3+}$  emission to the range of interest. Combinations of La-Gd, La-Y, La-Lu may be necessary.

The large size of the  $\text{Ce}^{3+}$  generally leads to a low distribution coefficient ( $k$ ) in Y or Lu analogs. The values are sometimes as low as 0.1-0.2. For  $\text{Gd}_2\text{SiO}_5$ ,  $k$  increases to about 0.4-0.5. If the  $\text{La}_2\text{SiO}_5$  analog can be made, the  $k$  values are very close to 1. However, with the low dopant levels of  $\text{Ce}^{3+}$  (0.1%) which are needed, there is not much difficulty in the phase behavior or crystal growth. We fully expected that  $\text{Ce}^{3+}$  could be introduced in low amounts (0.1%) in all crystals such as La, Gd, Y, or Lu compounds and so far this has been borne out.

Seed orientation plays a large part in both the crystal growth and the resulting laser properties. For noncubic materials, there may be serious reasons for investigating the optimum direction for growth. Similarly the polarization properties of emitted light are a topic for their efficient use in any laser. It has also been reported that the  $\text{R}_2\text{SiO}_5$  type silicates have a possible plane of separation, and this has been observed in our growth runs for the  $\text{Gd}_2\text{SiO}_5$  composition. However, this does not seem to be true for the  $\text{Y}_2\text{SiO}_5$  crystalline material and only mildly so for the mixed composition  $(\text{Gd/Y})_2\text{SiO}_5$ .

Our preliminary effort concentrated on the growth of large single crystals, doping, orientation, crystal structure effects, and finally the mechanical processing of any grown crystals.

The primary objective was the growth, but closely tied to this were physical studies on the absorption, fluorescent emission, lifetime, polarization, and other laser parameters. Most of the latter is to be done at the Naval Research Laboratory.

### 3.1 Phase Diagrams

A thorough examination of the available relevant phase diagrams (from the A.C.S.'s "Phase Diagrams for Ceramists" series) for the  $R_2O_3$ - $SiO_2$  systems (where R is a rare earth) show that the phase diagrams exhibit similar structure especially around the one to one molar percent ratio line. The existence regions for the  $R_2SiO_5$  compositions are bounded by solidus and liquidus curves and two eutectics around the 1:1 line. This can be seen in Figure 1 of the introductory section to this report. The temperature ranges of these existence regions are also very closely centered around 1900°C. This would indicate that  $R_2SiO_5$  single crystal material should be isostructural as R is varied allowing mixed composition single crystal boules to be pulled stoichiometrically from the melt.

### 3.2 Doping and Atmosphere Control

The crystals grown in this series of experiments were doped by adding  $CeO_2$  at about the 0.1% level of the precursor powder mixture. Conversion from  $Ce^{+4}$  to  $Ce^{+3}$  is thought to have been incomplete in the early growth runs. This was revealed by a yellowish coloration in portions of the melt and crystals. There was, however, always sufficient conversion to cause a very bright luminescence under UV illumination. More complete conversion appeared to be achieved in later runs by going from a flowing

atmosphere of  $N_2$  and forming gas to just a flowing  $N_2$  gas cover.

### 3.3 Experimental Runs

The basic experimental conditions of each of the growth runs performed during this period are outlined in Table I. Three experimental runs were performed during this period each with the intent of providing insight into the shifting of the  $Ce^{+3}$  luminescence peak position with variation in the rare earth ion environment. Another goal was to try and produce large single crystal pieces of the various compositions.

Run 21 was an attempt to seed a  $Y_2SiO_5$  melt with a  $Gd_2SiO_5$  seed. This was basically a repeat of Run 19 but more time was allowed for mixing and the melt was also stirred with an iridium rod. Seeding was very difficult as burn off kept occurring and when growth was finally initiated the boule turned out to be composed of fine polycrystallites. The next few attempts at seeding resulted in complete dissolution of the seed. A new seed was installed and after a few attempts seeding was successful and a short, very thin crystalline rod was pulled. This was then left in contact with the melt during cooldown to promote crystallization of the melt. This succeeded and some sizeable pieces were extracted from the crucible mass. During extraction of the crucible mass the technician doing the work observed bluish-purple flashes of light emanating from the crystalline material. It is suspected that this might be due to triboluminescence from strain relief of the crystal structure as it was broken. To try and test this hypothesis the cathodoluminescence of a single crystal piece of the

$\text{Y}_2\text{SiO}_5:\text{Ce}^{+3}$  and a powdered sample of the same were measured. The single crystal cathodoluminescence peaked at 414nm while the powdered sample's spectrum peaked at 420nm. This may indicate the presence of a strain induced shift in the crystal field.

Run 22 involved attempts to seed an  $\text{La}_2\text{SiO}_5:\text{Ce}^{+3}$  melt with both  $\text{Gd}_2\text{SiO}_5$  and  $\text{Y}_2\text{SiO}_5$  seeds. This run was a repeat of Run 20 with increased time allowed for mixing and additional stirring with an iridium rod. As in Run 20 the seeds kept burning off so an iridium wire was used to initiate growth which resulted in a small boule which was left in contact with the melt during cooldown to stimulate crystallization of the melt. The boule was aquamarine in color while the crucible mass was composed of greenish polycrystallites indicating a contaminant in the melt. After core drilling, the crucible mass showed a large degree of segregation with the presence of  $\text{Ce}^{+4}$  indicated in the lower regions. Neither the boule nor the crucible mass exhibited luminescence under UV illumination indicating that the desired phase is probably not present. The crucible mass also hydrated to a powder form after a few days.

Run 23 was performed to see if a mixed Gd/Y silicate could be grown. A  $\text{Gd}_2\text{SiO}_5$  seed was used to pull a boule from a melt of composition  $\text{GdYSiO}_5:\text{Ce}^{+3}$ . The boule was grown to a length of about 82mm although only the first 62mm was crystalline (See Figure 5). The diameter was approximately 31mm and the surface was textured like the bark of a tree with vertical striations and some crazing. The boule and a good portion of the crucible mass were water white transparent crystals

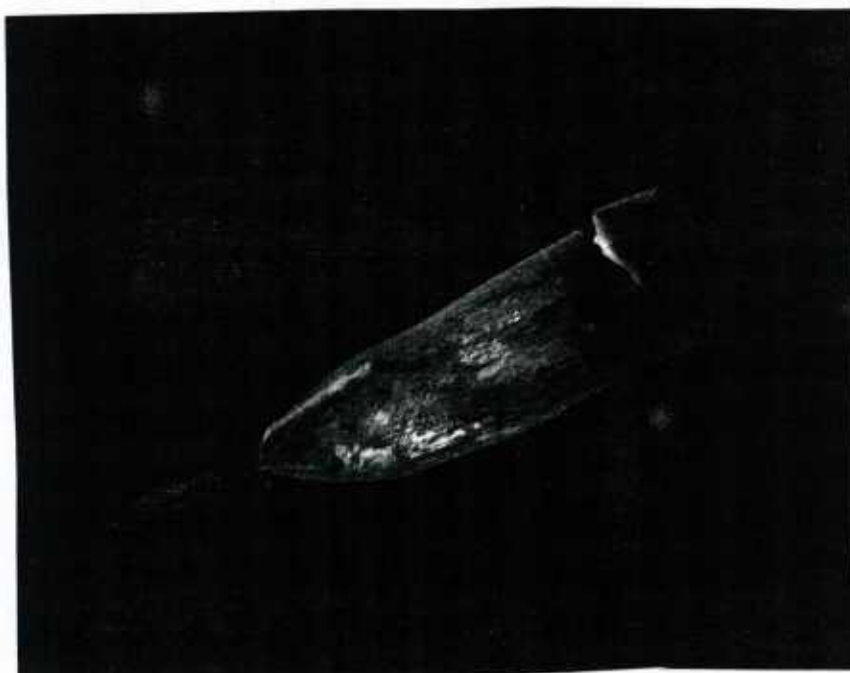


Figure 5  $(\text{Gd}_2\text{SiO}_5) : \text{Ce}^{+3}$  Boule Grown  
In Run 523

that fluoresced under UV illumination. Three samples were taken from this run for atomic absorption (A.A.) analysis to determine the relative Gd/Y ratios in the boule, the crystalline portion of the crucible mass and the polycrystalline portion of the crucible mass. The results of this analysis were inconclusive because the samples could not be dissolved although a number of digestion techniques were used. The A.A. ratios obtained from the portions that did dissolve showed Gd:Y molar ratios of 0.67:1 for the boule sample and 0.71:1 for the polycrystalline crucible mass sample. The cathodoluminescence results gave a peak emission of 415nm for the boule and 435nm for the polycrystalline sample. Some cleavage plane behavior was observed in the boule samples.

### 3.4 Cathodoluminescence Results

Samples from runs 21 and 23 exhibited bright luminescence from their  $\text{Ce}^{+3}$  content when exposed to UV radiation. Measurements using the e- beam cathodoluminescence apparatus gave luminescence spectrums showing the typical broad band  $\text{Ce}^{+3}$  profile. Shifts observed were similar to previously measured samples of the same composition.

### 3.5 Optical and Laser Evaluation

A sample from Run 21 was sent to the NRL shortly after the period covered by this report. A sample from Run 23 was not sent due to difficulties encountered in its fabrication. Results from NRL tests will indicate whether the material from Run 21 is a suitable candidate for laser material.

Table I  
List of Experimental Runs

<u>Run #</u>	<u>Iridium Crucible Size</u>	<u>Cover Gas</u>	<u>Pull &amp; Rotation Rates</u>	<u>Run Duration</u>	<u>Other Run Parameters</u>
21	3" x 3"	N	24 RPM .025"/hr	15 days	$\text{Y}_2\text{SiO}_5:\text{Ce}^{+3}$ melt $\text{Gd}_2\text{SiO}_5$ seeds
22	3" x 3"	N	24 RPM .025"/hr	19 days	$\text{La}_2\text{SiO}_5:\text{Ce}^{+3}$ melt $\text{Gd}_2\text{SiO}_5$ & $\text{Y}_2\text{SiO}_5$ seeds
23	3" x 3"	N	24 RPM .04"/hr.	8 days	$\text{GdYSiO}_5:\text{Ce}^{+3}$ melt $\text{Gd}_2\text{SiO}_5$ seed

Run Results

- 21 - Seed kept burning off, first boule all fine polycrystallites, redipped and pulled very small diameter boule, crystallized out melt by cooling it in contact with boule, most of crucible mass water white transparent crystal.
- 22 - Gd and Y silicate seeds kept burning off so iridium wire used to seed melt, a small boule was pulled and cooled in contact with melt to initiate crystallization of melt. Both boule and crucible mass have greenish coloration, crucible mass hydrated after a few days, boule was stable.
- 23 Grew boule 82mm long by 31mm diameter, water white transparent mostly single crystal for first 62mm, remaining portion was fine polycrystalline, top portion of melt crystalline, boule showed some cleavage plane behavior.



#### 4.0 Conclusions

The work performed so far under this contract has served to point out the most productive direction for further research. We now know that  $\text{Ce}^{+3}$  exhibits a very high luminescent activity in a wide range of  $\text{R}_2\text{SiO}_5$  compounds when present at about the 0.1% level. We have also observed shifts in the  $\text{Ce}^{+3}$  cathodoluminescent spectrum due to compositional substitution of the rare earth component of the orthosilicate structure. The wavelength shift from  $\text{R} = 100\% \text{ La}$  to  $\text{R} = 100\% \text{ Lu}$  may be as much as 50 to 70nm. One objective now is to optimize compositions so as to produce the desired emission spectrum together with exploration of other orthosilicate systems which may broaden the available wavelength range.

Growth of a small boule of  $\text{GdYSiO}_5$  has been successfully undertaken during this report period. The goal now is to extend the growth techniques acquired to date to produce larger, more perfect boules of  $\text{Gd}_2\text{SiO}_5$  for laser rod fabrication. This can then be adapted easily to other orthosilicate systems for production of large boules from these materials as well.

## References

1. See previous reports and data of Contract N00014-81-C-0656 and N00014-83-C-0072 by Airtron Division of Litton; other contractors such as EIC Laboratories, Crystal Systems, Inc., and MIT have obtained similar results in parallel programs under ONR.
2. J. Felsche is "Structure and Bonding", Vol. 13, p. 99 (Springer-Verlag, New York, 1973).
3. Phase Diagrams for Ceramists, 1969 Supplement, American Ceramic Society, Figure 2367.
4. G. Buisson and C. Michel, Mat. Res. Bull. 3, 193 (1968).
5. L. A. Harris and C. B. Fuich, Amer. Mineral. 50, 1493 (1965).
6. I. A. Bondar, L. N. Koroleva, and N. A. Toropov, Rost, Kristallov. Akad Nauk SSSR Ins. Krist 6, 111 (1965).
7. I. A. Bondar, L. N. Koroleva, and D. P. Sipovskii, Russ. J. Inorg. Chem. 13, 1635 (1968).
8. B. M. Wanklyn F. R. Wondre, G. B. Ansell, W. Davison, J. Mat. Sci. 9, 2007 (1974).
9. Kh. S. Bagdasarov, A. A. Kaminskii, A. M. Kevorkov, A. M. Prohkorov, S. E. Sarkison, T. A. Tevosyon, Soviet Physics-Doklady 18, 664 (1973).
10. A. A. Kaminskii, et al., Inorganic Materials (USSR) 12, 1238 (1976).
11. K. Takagi and T. Fukazawa, Appl. Phys. Letters 42, 43 (1983).
12. J. Pistorius, Philips Laboratory, Eindhoven, The Netherlands, 1984.

APRIL 1984

REPORTS DISTRIBUTION LIST FOR ONR PHYSICS DIVISION OFFICE  
UNCLASSIFIED CONTRACTS

Director Defense Advanced Research Projects Agency Attn: Technical Library 1400 Wilson Blvd. Arlington, Virginia 22209	1 copy
Office of Naval Research Physics Division Office (Code 412) 800 North Quincy Street Arlington, Virginia 22217	2 copies
Office of Naval Research Director, Technology (Code 200) 800 North Quincy Street Arlington, Virginia 22217	1 copy
Naval Research Laboratory Department of the Navy Attn: Technical Library Washington, DC 20375	1 copy
Office of the Director of Defense Research and Engineering Information Office Library Branch The Pentagon Washington, DC 20301	1 copy
U.S. Army Research Office Box 1211 Research Triangle Park North Carolina 27709	2 copies
Defense Technical Information Center Cameron Station Alexandria, Virginia 22314	12 copies
Director, National Bureau of Standards Attn: Technical Library Washington, DC 20234	1 copy
Director U.S. Army Engineering Research and Development Laboratories Attn: Technical Documents Center Fort Belvoir, Virginia 22060	1 copy
ODDR&E Advisory Group on Electron Devices 201 Varick Street New York, New York 10014	1 copy

Air Force Office of Scientific Research Department of the Air Force Bolling AFB, DC 22209	1 copy
Air Force Weapons Laboratory Technical Library Kirtland Air Force Base Albuquerque, New Mexico 87117	1 copy
Air Force Avionics Laboratory Air Force Systems Command Technical Library Wright-Patterson Air Force Base Dayton, Ohio 45433	1 copy
Lawrence Livermore Laboratory Attn: Dr. W. F. Krupke University of California P.O. Box 808 Livermore, California 94550	1 copy
Harry Diamond Laboratories Technical Library 2800 Powder Mill Road Adelphi, Maryland 20783	1 copy
Naval Air Development Center Attn: Technical Library Johnsville Warminster, Pennsylvania 18974	1 copy
Naval Weapons Center Technical Library (Code 753) China Lake, California 93555	1 copy
Naval Underwater Systems Center Technical Center New London, Connecticut 06320	1 copy
Commandant of the Marine Corps Scientific Advisor (Code RD-1) Washington, DC 20380	1 copy
Naval Ordnance Station Technical Library Indian Head, Maryland 20640	1 copy
Naval Postgraduate School Technical Library (Code 0212) Monterey, California 93940	1 copy
Naval Missile Center Technical Library (Code 5632.2) Point Mugu, California 93010	1 copy

Naval Ordnance Station Technical Library Louisville, Kentucky 40214	1 copy
Commanding Officer Naval Ocean Research & Development Activity Technical Library NSTL Station, Mississippi 39529	1 copy
Naval Explosive Ordnance Disposal Facility Technical Library Indian Head, Maryland 20640	1 copy
Naval Ocean Systems Center Technical Library San Diego, California 92152	1 copy
Naval Surface Weapons Center Technical Library Silver Spring, Maryland 20910	1 copy
Naval Ship Research and Development Center Central Library (Code L42 and L43) Bethesda, Maryland 20084	1 copy
Naval Avionics Facility Technical Library Indianapolis, Indiana 46218	1 copy